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Great Lakes Science Advisory Board. Annual Report 1983. Appendix 1: Atmospheric Pollution Indicators

Great Lakes Science Advisory Board. Atmospheric Pollution Indicators Task Force

Great Lakes Science Advisory Board
Report to the International Joint Commission

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We have the 1983 annual report (GLC ZZ... IJC.10 ..AS6 ENG 1983) but not the appendices.

1983 Annual Report

Appendix I

Atmospheric Pollution Indicators

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1983 Annual Report

Appendix I

Atmospheric Pollution Indicators

Prepared by the
Atmospheric Pollution Indicators Task Force
of the Science Advisory Board
of the International Joint Commission

February 1985
Windsor, Ontario

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PREFACE

This is Appendix I of the Science Advisory Board's 1983 Annual Report. It includes two reports on the atmospheric pollution indicators issue - one prepared by the Board's Atmospheric Pollution Indicators Task Force and the other by a Contractor. The Contractor's report was prepared with funds provided by the Board, under the direction of the Board's Atmospheric Pollution Indicators Task Force. Any viewpoints contained therein should not necessarily be construed as those of the Great Lakes Science Advisory Board or the International Joint Commission. The Board's conclusions and recommendations on the Atmospheric Pollution Indicators issue are contained in the Board's 1983 Annual Report to the Commission.

Copies of the Science Advisory Board's 1983 Annual Report may be obtained from the International Joint Commission at the Great Lakes Regional Office in Windsor, Ontario, Canada.

ACKNOWLEDGEMENTS

The Task Force is indebted to all those who have directly or indirectly contributed to the completion of this Appendix.

Sincere appreciation is extended to the correspondents - Dr. J. Hulston (Institute of Nuclear Sciences, New Zealand), Professor Henry Schwarcz (Geology Department, McMaster University) and Professor M. Stuiver (Quaternary Isotope Laboratory, U. of Washington) - for providing their viewpoints on the feasibility of using conservative substances as tracers of atmospheric pollution. The Task Force is especially thankful to Dr. Ben Holt (Argonne National Laboratory) and Professor Ian Kaplan (Institute of Geophysics and Planetary Science, UCLA) for providing their viewpoints on the atmospheric pollution indicators issue and for taking the time to review the two reports, and to Dr. Jerome Nriagu (National Water Research Institute, CCIW) for his enlightning conversations on the feasibility of using stable isotopes as tracers of atmospheric pollution sources.

Special thanks are extended to Mr. Robert Ceschan, of the Great Lakes Regional Office, for his assistance in preparing the draft of the Task Force's Report and for editing and organizing the Contractor's Report. Additionally, useful and constructive comments on the Task Force's Report were received from Dr. Bill Strachan (National Water Research Institute, CCIW) and Dr. Joel Fisher (International Joint Commission, Washington); to whom, the Task Force is specially grateful.

Finally, the Task Force would like to thank the contractor - Dr. Edward Rees - for a timely and comprehensive review and objective assessment of the stable isotope literature.

A. REPORT OF THE TASK FORCE

Over the past two decades, it has become increasingly apparent that the atmospheric deposition of pollutants to lakes is biologicaly and geochemically significant. The deposition of some airborne inorganic and organic pollutants is a sizeable, if not major, input source to the Great Lakes. Both the upper Lakes Reference Group and the Pollution from Land Use Activities Reference Group (PLUARG) recognized the significance of the atmosphere in the deposition of metals, nutrients, DDT and PCBs, while recent studies revealed the occurrences of many more compounds including TCDD, Toxaphene and PAHs.

The relative importance of atmospheric deposition of contaminants to the Great Lakes versus municipal and industrial point discharges is presented in Table 1 for cadmium and benzo(a)anthracene (a PAH).

TABLE 1. PRELIMINARY ESTIMATES OF CADMIUM AND BENZO(a)ANTHRACENE LOADINGS TO THE GREAT LAKES (METRIC TONNES PER YEAR)

	SOURCES					
	ATMOSPHERIC		MUNICIPAL		INDUSTRIAL*	
Lake	Cd	PAH	Cd	PAH	Cd	PAH
Superior	8.2	4.1	0.4	ND	8.1	0.7
Michigan	58.0	2.9	5.7	ND	870.0	112.0
Huron	60.0	3.0	5.7	ND	115.0	91.0
Erie	75.0	1.3	12.7	ND	725.0	144.0
Ontario	28.0	0.94	8.1	ND	725.0	31.0

* Incomplete Data
ND-Not Detected
Source: Great Lakes Science Advisory Board 1980 Annual Report: (a) Appendix A by Eisenrich, S.J., B.B. Looney and J.D. Thornton, on "Assessment of Organic Contaminants in the Great Lakes Ecosytem"; and (b) Appendix B by Allen, H.E. and M.A. Halley, on "Assessment of Airborne Inorganic Contaminants in the Great Lakes".

As is discernible from the Table, the atmospheric deposition of cadmium and benzo(a)anthracene is particularly pronounced relative to municipal and industrial sources for the Upper Great Lakes, notably Lake Superior. This is indicative of most other pollutants including various nutrients (phosphorus and nitrogen), metals (lead, mercury, and zinc) and trace organics (PCBs, and DDT). The combustion of fossil fuels constitutes the largest source of airborne organic and inorganic substances.

The importance of the atmospheric pathway to Great Lakes water quality is also denoted by the aerial extent of contamination by covering entire lake surfaces, and the deposited contaminants are in a state more likely to harm aquatic biota. Unlike tributary or shoreline erosion where most contaminants are sorbed into particulates, atmospheric contaminants can be in a more soluble and therefore available state.

Sources of airborne pollutants to the Great Lakes include a mosaic of local, regional and global long-range origins. Emitted gas or particulates can travel hundreds if not thousands of kilometers. The relative abundances of materials contributed to the Great Lakes, from a wide array of sources, would be dependent upon a number of variables including emission stack height, meteorological conditions (e.g. prevailing direction and magnitude of winds), the physical and chemical characteristics of the emitted particulate or gaseous material, and quantities released.

The subsequent monitoring and identification of sources of atmospheric pollutants deposited to the Great Lakes, poses a formidable and virtually impossible task. Atmospheric monitoring, as it presently stands, can give only crude estimates of atmospheric loadings. Land-based bulk and wet deposition samplers are stationed on islands, along shorelines, or on nearshore structures where the wind regime differs from open lakes and most likely would not provide representative estimates of actual atmospheric loadings to the open lakes.

There is a need to adopt some tool for deducing the relative proportions of materials deposited into the Great Lakes from the various sources. Such an indicator(s) must be stable during transport away from the emission source.

Emitted organic pollutants, for example, may undergo some degree of photodegradation or chemical transformation while in the airborne stage. Similarly, inorganic pollutants may be oxidized. Stable isotopes which have been used sparingly to better understand lake processes, for example, might meet this criteria. Stable isotope variations have been used in the past as tracers and to show that relationships can exist between in-lake contaminants and different sources of pollution.

Recognizing the possible utility of such a tool in determining the relative proportion of materials derived from atmospheric sources, the Great Lakes Science Advisory Board in their 1982 Annual Report recommended that:

> "more research effort be directed toward the identification of conservative indicators of atmospheric inputs of toxic materials into the Great Lakes".

In 1983 the Science Advisory Board established a Task Force on Atmospheric Pollution Indicators to report on the feasibility of using conservative indicator substances as tracers of atmospheric pollution sources, and to identify specific research needs.

The initial activity of the Task Force was to request feedback and advice from a select group of geochemists on the feasibility of utilizing conservative substances as tracers of atmospheric pollution. The respondents generally indicated that while the use of indicator substances potentially provides a feasible tool for indicating sources of atmospheric pollution, a great deal of prior work would be needed because of large spatial and temporal variations and the multitude of possible pollution sources experienced by the Great Lakes. A summary of the responses received is provided below.

Dr. Ben Holt (Argonne National Laboratory) indicated that using conservative substances for tracing sources of atmospheric deposition to the Great Lakes might be feasible, although their studies have shown that the usefulness of oxygen isotope ratio measurements is precluded by rapid isotopic exchange between SO_2 and ambient water.

Professor Ian Kaplan (Department of Geochemistry, University of California), while not discouraging the use of conservative indicators of

pollution, suggested that a great deal of prior work would have to be performed beforehand. Large seasonal and regional variations of pollution inputs to lakes need to be considered, while isotopic ratios, for example, could overlap if derived from various sources. Organic tracers, such as polynuclear aromatic hydrocarbons or organic nitrogen compounds which are unique to the atmosphere, may prove to be more useful indicators in the Great Lakes. The insoluble residues extracted from suspended particles in the water body could be microscopically and chemically analyzed to determine their origins.

Both Drs. C.E. Rees and H.P. Schwarcz (Department of Geology, McMaster University) are currently engaged in studies investigating the use of stable sulphur and oxygen isotopes (in acid precipitation) which would possibly allow clearer discrimination of sources of atmospheric loadings. Based on work by Krouse, Dr. Schwarcz further noted that the identification of pollution sources based strictly on $^{34}S/^{32}S$ isotope ratio would be impossible because of species overlap in fossil fuels. Such ratios, however, would add to the total skein of evidence necessary to locate a source of pollution.

Drs. Schwarcz and Rees also indicated that difficulties would be encountered in applying such studies to the Great Lakes due to the complexity of the hydrochemical system, the multiple pollution inputs, and that the pattern of loadings must be deduced over extensive geographical areas. Such an endeavour would require a far greater degree of effort than previous studies of a similar nature. This would include large-scale sampling over the entire Great Lakes and over a sufficient period of time to permit pinpointing seasonal and long-term fluxes, and respective variations in isotopic ratios.

The remaining two respondents, Professor M. Stuiver (Quaternary Isotope Laboratory, University of Washington) and Dr. R. Hulston (Institute of Nuclear Sciences, New Zealand Department of Scientific and Industrial Research), did not have any specific suggestions regarding the feasibility of utilizing conservative substances as pollution indicators to the Great Lakes because of lack of experience in the subject area.

Given the ambiguous statements provided by the respondents and the need to resolve the feasibility issue, a better understanding of the issue was needed before any merit could be placed in the application of such tools to the Great Lakes. Subsequently, a contract was awarded to a specialized geochemist to provide a scientific overview of the issue by reporting on the state of the science to assist the Task Force in their deliberations on the feasibility of utilizing such conservative indicators for deducing atmospheric sources of pollution to the Great Lakes.

The remainder of the report presents the contractor's overview on the feasibility of using stable isotopes as tracers of the sources of atmospheric pollution in the Great Lakes Basin. Any viewpoints contained therein should not be construed as those of the Task Force or of the Great Lakes Science Advisory Board.

B. REPORT OF THE CONTRACTOR

THE FEASIBILITY OF USING STABLE ISOTOPES AS TRACERS OF THE SOURCES OF ATMOSPHERIC POLLUTION IN THE GREAT LAKES BASIN: AN OVERVIEW

by

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1. INTRODUCTION

On 29 June 1983, the National Research Council of the U.S.A. issued a report on "Acid Deposition: Atmospheric Processes in Eastern North America". One conclusion was that no method yet exists of estimating the relative contributions of particular sources to the pollution level found at particular locations (Marshall, 1983).

Concentration measurements alone do not provide information on the original source(s) of a measured parameter. But if it could be shown that a measured parameter is source specific, this parameter could potentially be used as a tracer methodology for deducing sources of pollution. Sulphur dioxide, for example, can be characterized by a distinct isotopic signature. This signature could, therefore, be a useful indicator of the sulphur source. Consequently, this report examines the feasiblity of using isotopic measurements for deducing the relative contributions of airborne contaminants from differing sources to the Great Lakes.

Emphasis of the report is on the use of sulphur, oxygen and lead isotopic measurements. Such measurements are particularly relevant to the determination of sources of elements in atmospheric samples as well as

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Marshall, E. 1983. Acid rain, a year later. Science 221: 241-242.

precipitation and water. Although nitrogen isotopes have been used for determining water pollution from the addition of fertilizer material or industrial waste to land, it has little applicability in atmospheric investigations.

Other conservative indicator substances as tracers of atmospheric sources of pollution are also not discussed. Nickel/vanadium ratios, for example, are more applicable for the determination of sources of oil in oil spills than in atmospheric studies.

This overview considers ways in which stable isotopes may be used as potential indicators of atmospheric pollution in the Great Lakes Basin. A brief description of isotopes and their abundance variations is given since this method is not as fully understood as other pollution monitoring methodologies. This is followed by a summary of sulphur isotope abundances in nature and anthropogenic contributors to atmospheric sulphur.

Section 6 summarizes the findings and conclusions of two sulphur isotope studies conducted in the Great Lakes Basin. Sections 7 and 8 respectively discuss ways in which oxygen and lead isotopes are used in pollution studies. Based on the information presented in the preceding sections, the final section presents remarks on the feasiblity of using the stable isotopes of sulphur, oxygen and lead as indicators of the sources of atmospheric pollution in the Great Lakes Basin.

Bibliographies are appended to individual sections which list the studies cited. Additionally, other pertinent investigations having a direct bearing on the subject matter were included for reference purposes.

2. ISOTOPE ABUNDANCE VARIATIONS

Isotopes are atoms whose nuclei contain equal numbers of protons but different numbers of neutrons and therefore vary in mass. Thus, isotopes occupy the same position in the periodic table of elements. Most of the naturally occurring elements, except for twenty-one, are mixtures of two or more stable isotopes. The elements considered in this report - sulphur, oxygen and lead - each have a number of stable isotopes.

Sulphur or element number 16 (i.e. the element whose atoms have 16 protons in their nuclei), has four stable isotopes which appear in the following approximate relative abundances:

$^{32}_{16}S^{16}$~95%; $^{33}_{17}S^{16}$~0.8%; $^{34}_{18}S^{16}$~4.2%; $^{36}_{20}S^{16}$~0.017%.

The symbols for the isotopes are written in their full form, for example, a sulphur isotope with a relative atomic mass of 33, contains 16 protons (as do all the sulphur isotopes) and 17 neutrons in the nucleus.

Oxygen or element number 8, has three stable isotopes and the following approximate relative abundances:

$^{16}_{8}O^{8}$~99.76%; $^{17}_{9}O^{8}$~0.04%; $^{18}_{10}O^{8}$~0.2%.

Lead or element number 82, has four stable isotopes and the following relative abundances:

$^{204}_{122}Pb^{82}$~1.5%; $^{206}_{124}Pb^{82}$~23.6%; $^{207}_{125}Pb^{82}$~22.6%; $^{208}_{126}Pb^{82}$~52.3%.

The relative isotope abundances of those elements, as well as others, are highly variable in nature. Such variations arise in terrestrial samples either because of chemical or physical processes, or variable contributions over time from the radioactive decay of isotopes of other elements.

Given the different numbers of neutrons in the nuclei of isotopic atoms and hence different masses, isotopes and compounds containing different isotopes have different physical and chemical properties. The element hydrogen, for example, has two stable isotopes ^{1}H and ^{2}H (often written as D). Their mass difference is 100± and the chemical differences between the two isotopes and affiliated compounds are extreme. For heavier elements, the mass differences between isotopes are smaller. The mass difference for the isotope pair ^{16}O-^{18}O is 12% and for ^{32}S-^{34}S it is 6%, therefore the physical and chemical differences between the isotopes of oxygen and sulphur, are much smaller than the isotopes of hydrogen. Regardless, these heavier elements are readily detectable with modern high precision spectrometric techniques.

Processes which produce changes in isotopic composition, or isotope fractionation, can be subdivided into unidirectional and equilibrium processes. In an undirectional process, such as a one step chemical reaction or evaporation from a liquid, isotope fractionation occurs because light isotopic species react more rapidly than heavy species of the same element or compound. The preferential reaction of a light isotopic species causes the product material to have a higher relative abundance of that isotope than the original starting material. Similiarly, the residual unreacted material becomes depleted in the light isotopic species relative to the original starting material because of the preferential reaction.

In equilibrium processes, as in the analogous case of chemical equilibria, the light and heavy isotopes of an element adopt a distribution which minimizes the free energy of the system between the compounds present in the equilibrating system. In practice, isotopic equilibrium is established if reaction pathways are present that allow the exchange of isotopes between the various components of the system. In the majority of isotopic exchange reactions, the equilibrium configuration is one in which the light isotopes are enriched in low oxidation states and the heavy isotopes are enriched in high oxidation states within the element in question.

As mentioned earlier, a number of elements, including lead, show variations in their isotope abundance patterns due to the radioactive decay of other elements. With lead, the following radioactive decay sequences are involved:

$$^{238}U \rightarrow {}^{206}Pb + 8He + 6\beta^-$$

$$^{235}U \rightarrow {}^{207}Pb + 7He + 4\beta^-$$

$$^{232}Th \rightarrow {}^{208}Pb + 6He + 4\beta^-$$

Thus the isotopic composition of lead can be altered by the presence of uranium and thorium. The isotopic composition of lead in a particular sample depends on the amount and isotopic composition of the lead originally present, the amounts of uranium and thorium present and the time available for their decay to lead.

This decay scheme forms the basis of the uranium/thorium dating method whereby the isotopic composition of lead can be used to estimate the time elapsed since the emplacement of geological systems. The known half-lives of the radioactive uranium and thorium, combined with the measurement of these concentrations and lead isotopic compositions, lead to an estimate of time during which the decay process has occurred. It also serves as the basis by which the isotopic composition of lead can be used as a tracer of its origin.

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3. SULPHUR ISOTOPE ABUNDANCE VARIATIONS IN NATURE

Although sulphur has four stable isotopes, the variations in sulphur isotope abundances are invariably expressed in terms of the isotope abundance ratio $^{34}S/^{32}S$. Furthermore, variations of this ratio are expressed in the 'del' notation:

$$\delta^{34}S, ‰ = \left[\frac{(^{34}S/^{32}S)\text{sample}}{(^{34}S/^{32}S)\text{standard}} - 1 \right] \times 1000$$

where "‰" or "permil", signifies parts per thousand and where the accepted standard is sulphur from the troilite phase of the Canyon Diablo meteorite for which the $^{34}S/^{32}S$ value is taken to be 0.0450045 (Thode and Rees, 1970).

The total range of $\delta^{34}S$ values encountered in nature is from about -65‰ to +95 ‰ indicating a total range of variation of $^{34}S/^{32}S$ of ~160‰ (Faure, 1977). The extreme values in this range are encountered very rarely. A more reasonable range for practical purposes is probably from -60‰ to +60‰ (Nielsen, 1979). Figure 1 shows the ranges of $\delta^{34}S$ values found in various types of geological environment.

As can be seen, meteoritic sulphur lies close to $\delta^{34}S = 0$ as does the sulphur from igneous rocks. Volcanic sulphur shows a wider range of isotopic compositions, more or less symmetrically around $\delta^{34}S = 0$. The widest variations are exhibited by sedimentary sulphides which tend to have negative $\delta^{34}S$ values. Conversely, sedimentary sulphates almost invariably have positive $\delta^{34}S$ values while the sulphate in modern seawater is very uniform at +21‰.

The isotopic composition of sulphur in rivers, lakes and precipitation is variable and depends on a number of factors, including anthropogenic input (to be discussed later).

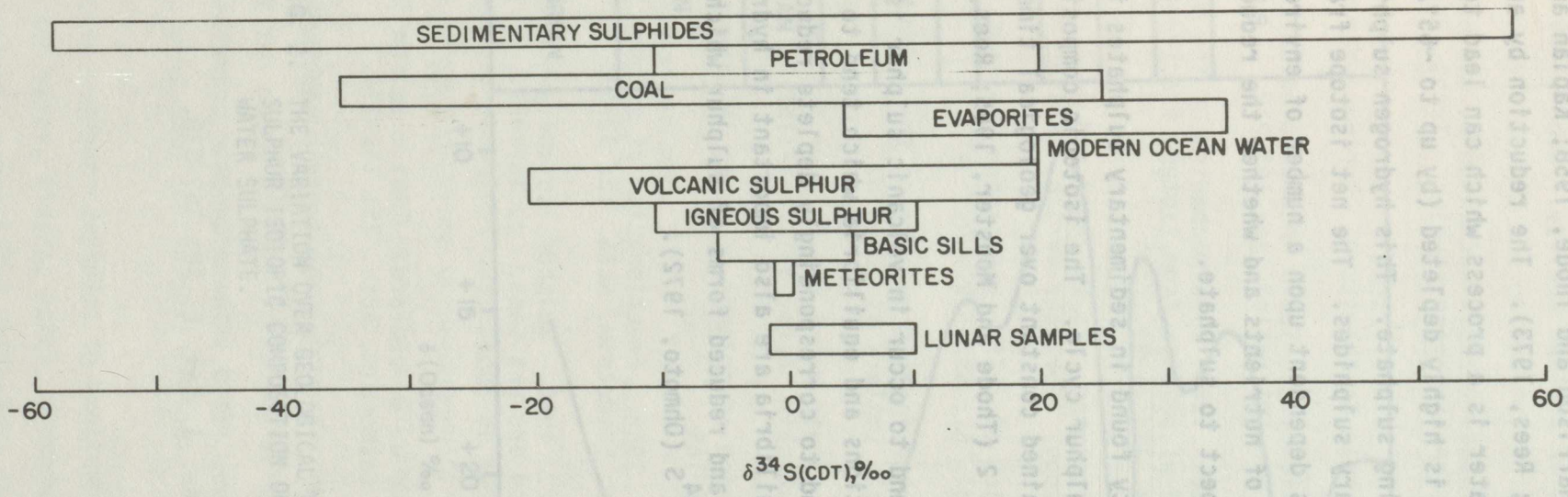

FIG. 1. THE DISTRUBUTION OF SULPHUR ISOTOPES IN NATURE

The major agent responsible for variations in $\delta^{34}S$ values is the biological sulphur cycle (Harrison and Thode, 1958; Kaplan and Rittenberg, 1964; Kemp and Thode, 1968; Rees, 1973). The reduction by anaerobic bacteria of sulphate dissolved in water is a process which can lead to the production of hydrogen sulphide which is highly depleted (by up to ~65‰) in $\delta^{34}S$ relative to the starting sulphate. This hydrogen sulphide can react with iron to form sedimentary sulphides. The net isotope fractionation manifested in a sediment is dependent upon a number of environmental factors including the availability of nutrients and whether the reduction environment is open or closed with respect to sulphate.

The isotopic variability found in sedimentary sulphates is also indirectly linked to the biological sulphur cycle. The isotopic composition of ocean water sulphate has not remained constant over geological time but has varied in the manner shown in Fig. 2 (Thode and Monster, 1965; Rees, 1970).

The range of values found to occur in volcanic sulphur is due to a variety of inorganic chemical reactions and equilibria which tend to enrich oxidised forms of sulphur in $\delta^{34}S$ and to correspondingly deplete reduced forms. Inorganic reactions and equilibria are also important in hydrothermal fluids and again lead to oxidised and reduced forms of sulphur which are respectively enriched and depleted in $\delta^{34}S$ (Ohmoto, 1972).

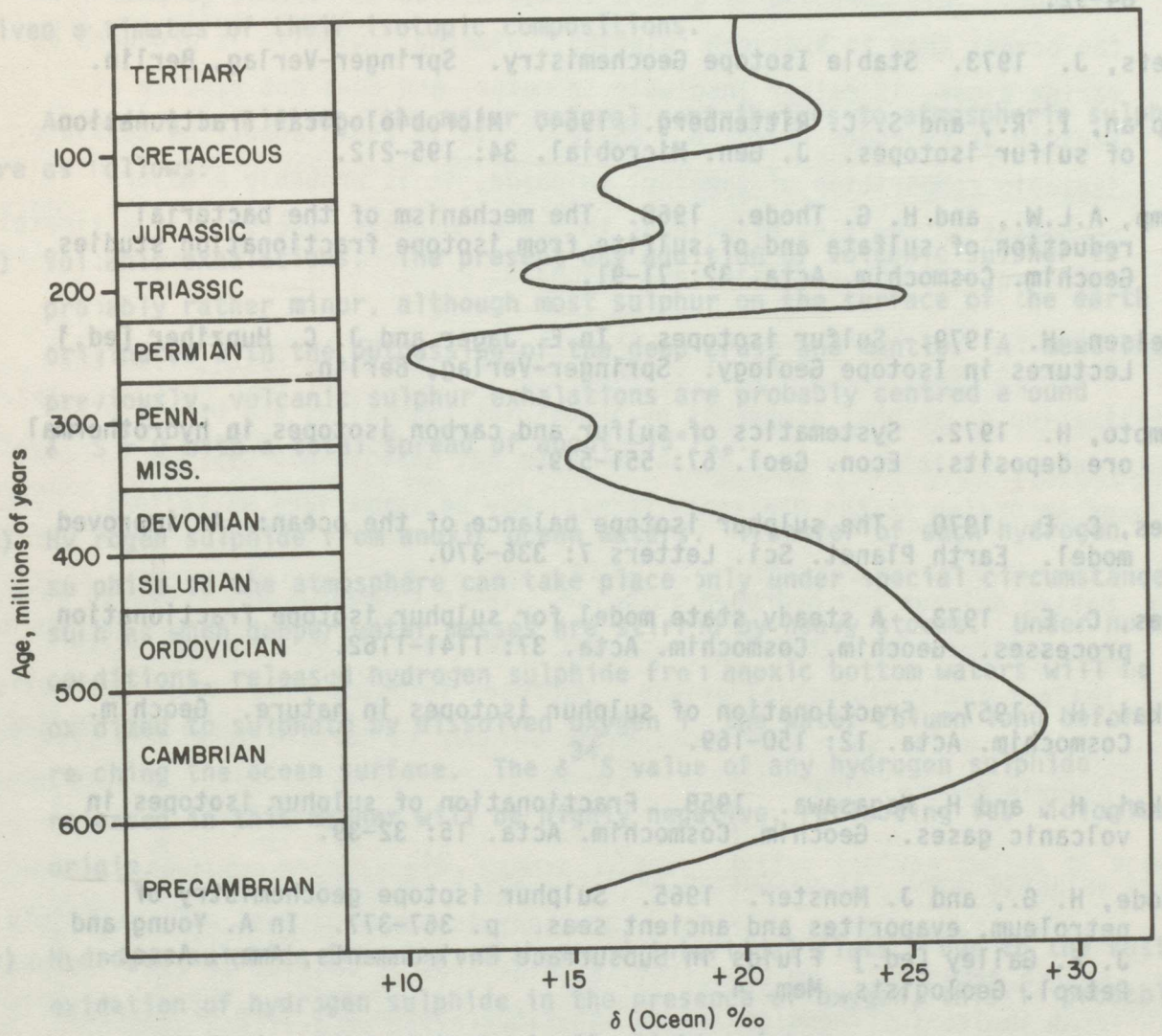

FIG. 2. THE VARIATION OVER GEOLOGICAL TIME OF THE SULPHUR ISOTOPIC COMPOSITION OF OCEAN WATER SULPHATE.

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4. SULPHUR ISOTOPES IN THE ATMOSPHERE

The isotopic composition and the concentration of sulphur in the atmosphere can be highly variable and highly source dependent. Nielsen (1973) has summarized the major contributors to atmospheric sulphur and in addition has given estimates of their isotopic compositions.

According to Nielsen, the major natural contributors to atmospheric sulphur are as follows:

a) Volcanic exhalations. The present day addition of volcanic sulphur is probably rather minor, although most sulphur on the surface of the earth originated with the outgassing of the deep crust and mantle. As mentioned previously, volcanic sulphur exhalations are probably centred around $\delta^{34}S = 0$ with a total spread of about ~15°/$_{oo}$.

b) Hydrogen sulphide from anoxic ocean waters. Transfer of such hydrogen sulphide to the atmosphere can take place only under special circumstances, such as when deeper water masses are stirred by heavy storms. Under normal conditions, released hydrogen sulphide from anoxic bottom waters will be oxidized to sulphate by dissolved oxygen in the water column long before reaching the ocean surface. The $\delta^{34}S$ value of any hydrogen sulphide released in this manner will be highly negative, reflecting its biological origin.

c) Hydrogen sulphide from sea marshes and intertidal flats. Due to the fast oxidation of hydrogen sulphide in the presence of oxygen, this is probably a rather minor source of isotopically light sulphur.

d) Sea Spray. Sulphate is transferred from the ocean to the atmosphere by wave action at the ocean surface producing aerosols. This sulphate has a $\delta^{34}S$ value of +21°/$_{oo}$, reflecting its ocean water source. It can be transported by wind onto continental regions.

e) Biogenic volatile sulphur compounds in continental areas. This sulphur is derived from rain water, rivers, lakes, groundwaters, etc., and as such will have an isotopic composition reflecting that of its source.

d) Petroleum. Although the isotopic composition of sulphur in petroleum is variable - see for example Thode and Rees (1973), the sulphur in particular oil reservoirs and horizons tends to be rather homogenous isotopically. In general the $\delta^{34}S$ of oils tends to be ~15°/₀₀ light relative to the corresponding ocean water value prevalent when the oil was being formed.

Thus the $\delta^{34}S$ value of a particular atmospheric sample reflects the averaging of many inputs. In particular cases, where one or two sources of sulphur predominate, it may be possible to identify these sources and assess their relative contributions.

A series of studies originating from the Brookhaven National Laboratory, Upton, New York, has demonstrated the usefulness of sulphur isotopes in tracing the sulphur emitted from power plants and the oxidation to sulphate of sulphur dioxide present in emission plumes. Newman et al. (1975), Forrest and Newman (1977a) and references therein give full details of these studies. A further paper by Forrest and Newman (1977b) gives details of an isotopic study of the Sudbury smelter plume.

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5. SULPHUR ISOTOPES AS POSSIBLE INDICATORS OF ATMOSPHERIC SOURCES OF POLLUTION WITHIN THE GREAT LAKES BASIN

In order that the relative contributions of two or more sources of sulphur to a particular reservoir may be evaluated, it is necessary to know:

i) the isotopic compositions of the individual sources; and
ii) the isotopic composition of the reservoir in question.

From a practical point of view, it is further necessary that the sulphur from the different sources be isotopically distinct. The extent to which this practical limitation of the method is satisfied, may be judged from the data presented in two important papers from the Canada Centre for Inland Waters.

Nriagu's (1975) study entitled "Sulphur Isotope Variations in Relation to Sulphur Pollution of Lake Erie", considers the sources of sulphur in Lake Erie and the mixing patterns of the various masses of water within the lake. Data on the isotopic composition of the various forms of sulphur in the lake sediments is also included.

The most important points to be gleaned from this study are in connection with the magnitudes of the various inputs to and outflows from the lakes, and their respective isotopic compositions together with the conclusion that anthropogenic sulphur accounts for between 60 and 70± of the total sulphate in the lake.

Nriagu lists the various inputs and outputs for the lake as shown in Table . The various flow figures are in units of 10^{10} g SO_4 per year while the figures for the Lake Erie waters represent the total sulphate contents in units of 10^{10} g SO_4. The total input and outflow figure of ~450 x 10^{10} g SO_4 per year, together with the total lake content of 1053 x 10^{10} g SO_4 indicate a flushing time for the system of a little over two years.

TABLE 2

SULPHATE AND $\delta^{34}S$ INPUTS AND OUTPUTS TO LAKE ERIE

Source/Sink	SO_4, $\times 10^{10}$ g	Mean $\delta^{34}S$ (‰)	$\delta^{34}S$ range (‰)
Lake Huron outflow	267.8	+ 6.4	4 to 7
Runoff	110.1	+ 4.8	-2 to 8
Precipitation	16.3	+ 6.0	2 to 10
Sewage and other industrial discharges	58.7	+ 2.2	--
Total input	452.9	+ 5.4	-2 to 10
Total outflow	438.8	+ 5.2	4 to 6
Lake Erie waters:			
Western Basin	50.2	+ 6.4	4 to 7
Central Basin	649.3	+ 5.2	4 to 6
Eastern Basin	353.1	+ 5.2	4 to 6
Organic Matter	0.426	same as lake	--
Total	1053	--	4 to 7

The major source of sulphate in the lake is clearly the outflow from Lake Huron. Runoff from rivers accounts for somewhat less and in addition has a mean $\delta^{34}S$ value which is somewhat lower. Precipitation is a rather minor source of sulphur (~4% of the total) and has a mean $\delta^{34}S$ value that is rather similar to that of the outflow from Lake Huron.

Sewage and other industrial discharges are estimated to contribute approximately 13± of the total sulphur input to the lake. The isotopic composition assigned to this input unfortunately is not measured, but has been estimated from the $\delta^{34}S$ values of the other inputs, their relative magnitudes, and the isotopic composition of the lake water as a whole. This particular input is the one that is most distinct isotopically, from the others, at least at face value. It is important to note, however, that all of the other inputs have ranges of $\delta^{34}S$ values associated with them rather than uniquely determined values. Thus the calculation of the $\delta^{34}S$ value of the industrial input at +2.2% has errors associated with it that are not easy to evaluate.

It is important to bear in mind that the outflow from Lake Huron and the runoff from the various contributing river systems each contain, albeit indirectly, precipitation sulphur as well as erosional sulphur. These inputs to the lake contain sulphur from various sources, and their isotopic compositions represent the mixing of the various $\delta^{34}S$ values of these sources.

Nriagu and Coker (1978) have investigated the isotopic composition of sulphur in precipitation within the Great Lakes Basin. Samples were taken at 23 stations within the basin and classified as either urban, rural, or remote. Sampling was continued over a period of 18 months so that seasonal variations could be seen and evaluated.

It was found that there was a distinct seasonal variation in the isotopic composition of the sulphur in the bulk precipitation samples. The seasonal pattern was essentially the same for urban, rural and remote stations in that $\delta^{34}S$ values during the winter months were generally about 4°/₀₀ higher than those in the summer months.

Nriagu and Coker point out that the seasonal $\delta^{34}S$ variations could be due to corresponding variations in the contributions of the different sources to the atmospheric sulphur burden and to changes in the mechanism of origin of the sulphur in precipitation. Sulphur concentration values for urban stations were in general higher than at rural and remote stations. There was not a clear cut seasonal variation of sulphur concentration for any of the different station types. The authors also present data on the sulphur dioxide concentrations in air at selected urban sites in the Great Lakes Basin. The sulphur dioxide concentrations, unlike the sulphur concentrations in precipitation, do show a seasonal variation, with higher values during the winter months.

The authors speculate that the high $\delta^{34}S$ values found in the winter months may be due to the effects of sulphur emissions from space heating, while the lower $\delta^{34}S$ values found in the summer months are due to the emission of sulphur from bacteriogenic sources. If this is the case, then the lack of any clear cut seasonal variation of sulphur concentration in precipitation implies that the loads from these seasonally varying sources are comparable in magnitude even though they differ in isotopic composition.

The authors suggest that their interpretation of the data needs to be confirmed by a study of the time dependent variation of $\delta^{34}S$ values of atmospheric sulphur in the Lake Erie Basin and a detailed inventory of the sources and fluxes of sulphur in the Basin.

It is apparent from the data presented in these two papers that the quantitative estimation of the various sources and sinks of sulphur in the Great Lakes Basin is a complex matter. Moreover, it is evident that the range of $\delta^{34}S$ values to be encountered in rivers, lakes, and precipitation is rather limited. As was pointed out at the beginning of this section, the unambiguous identification of the relative contributions of various sulphur sources, demands that there be a clear cut isotopic distinction betwen them.

In the present case, the isotopic signatures seem likely to be only subtly different rather than drastically so. This being the case, it can be seen that the use of sulphur isotope ratios as indicators of the sources of atmospheric pollution within the Great Lakes Basin requires a rather extensive data base. This data base would have to provide information from a wide network of sampling stations, on such factors as:

a) atmospheric sulphur dioxide and its isotopic composition;

b) atmospheric and particulate sulphate and its isotopic composition;

c) sulphur concentration and isotopic composition in rainwater;

d) the sulphur content and isotopic composition of river water and of industrial effluents.

All the above will have regional and seasonal fluctuations. The estimation of natural and anthropogenic sulphur fluxes and reservoirs requires for its quantification in the Great Lakes Basin a rather high level of sampling and analysis activity.

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6. OXYGEN ISOTOPES AS INDICATORS OF THE MODE OF FORMATION OF ATMOSPHERIC SULPHATE

Oxygen isotope abundance variations are widely used in stable isotope geochemistry as indicators of geological processes and sources of oxygen in a variety of geochemical reservoirs. Oxygen isotope abundance variations are expressed in the del notation where

$$\delta^{18}O,{}^{o}/_{oo} = \left[\frac{(^{18}O/^{16}O)\text{sample}}{(^{18}O/^{16}O)\text{standard}} - 1 \right] \times 1000$$

i.e. in the same manner as sulphur isotope abundance variations.

A group of workers from the Argonne National Laboratory in the United States has recently published the results of a series of studies which show that the oxygen isotopic composition of atmospheric sulphate can be a useful tracer of its origin.

The essence of the method (Holt et al. 1981, 1982) is that anthropogenic sulphate in the atmosphere can arise in two ways. Primary sulphate is formed by high temperature reaction of reduced sulphur with atmospheric oxygen in industrial combustion processes. This formation mode gives the sulphate a distinctive isotopic signature. Secondary sulphate, on the other hand, is formed by the low temperature oxidation of atmospheric sulphur dioxide, which may itself of course have been formed from the combustion of sulphides.

The oxygen isotope composition of secondary sulphate is distinctly different from that of primary sulphate, because the isotopic equilibration between sulphur dioxide and water in the atmosphere is very rapid (Holt et al. 1983). This leads to the oxygen isotopic composition of secondary sulphate being essentially controlled by the oxygen isotopic composition of atmospheric water.

Mixtures of primary and secondary sulphate lead to intermediate $\delta^{18}O$ values, which may be used to estimate the relative contributions of the two

sorts of sulphate. The Argonne group pointed out the importance of estimating these relative proportions in order to identify sources of sulphate loading and to formulate effective regulatory strategies. It is becoming clear that wet scrubbers are much more effective at removing sulphur dioxide than they are at removing primary sulphate. Thus the installation of scrubbers at sites where the predominant sulphur source is in the form of primary sulphate would not be an effective control measure.

The studies cited above, have shown that in the neighbourhood of Chicago, primary sulphates constitute from 10 to 40% of the total ambient sulphates. The primary sulphate in aerosol sulphates varied from about 10% in the summer to 30 to 40% in the winter. On the other hand, the primary sulphate fraction in precipitation did not show a strong seasonal variation, ranging from 20 to 30% throughout the year.

The authors point out that in the Chicago region, most of the residential and commercial heating is from natural gas, while electricity generation is from coal or nuclear fuels. These sources of power produce relatively less primary sulphate than oil combustion so that other areas, particularly the Northeast, may have considerably higher primary sulphate loadings than those found for the Chicago area.

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7. LEAD ISOTOPES AS INDICATORS OF SOURCES OF POLLUTION

As outlined in Section 2, the isotopic abundances of lead are variable in nature due to the contributions of ^{206}Pb, ^{207}Pb and ^{208}Pb from the radioactive decay of uranium and thorium. Measurement of lead isotope ratios thus provides information that may, under favourable circumstances, be used to identify the source of lead by comparing measured isotope ratios with those determined for lead ore bodies. Lead samples from different ore bodies will have characteristic isotopic compositions reflecting the different degrees for which radiogenic lead, from the decay of uranium and thorium, is present.

Lead in petroleum and from smelter operations can both give rise to atmospheric loading. Rainfall plus the washout of particulate matter can cause the transfer of this lead to soil, lakes, and ocean water. Isotopic studies of lead have dealt with atmospheric lead, lead in water and lead deposited in sediments.

Gulson et al. (1983), have reported the isotopic composition of lead in particulate matter collected on aerosol filters from the Sydney area in Australia. The observed isotope ratios - $^{208}Pb/^{206}Pb$, $^{207}Pb/^{206}Pb$ and $^{206}Pb/^{204}Pb$ - varied by up to 25% during the three year study period and the variations were related to variable mixing of lead derived from at least three sources. The particular conclusion of the study was that much of the lead in Sydney air is derived from motor vehicle emissions.

A study by Stukas and Wong (1981) has yielded information on the natural and industrial sources of lead in the coastal waters of British Columbia. The values of $^{206}Pb/^{207}Pb$ reported are distinctly different for oceanic water, water in fjords that receive lead from mine tailings, and for waters near urban centers. The authors conclude that the natural abundances of stable lead isotopes is a powerful tool in identifying lead sources and in tracing lead pathways in coastal waters. The information derived from the isotope ratios concerning the sources of the lead cannot be obtained by simply determing the concentrations of lead.

In the coastal waters studied by Stukas and Wong, some of the lead from mine tailings made its way to the ocean by freshwater runoff, while gasoline lead was presumably present initially in the atmosphere and made its way to the ocean by precipitation and/or runoff.

A study by Hirao and Mabuchi (1982) has used the isotope ratios of lead in the sediments of the Tokyo Bay in Japan to construct a historical record of the sources of pollutant lead in this area.

These three studies, as well as others cited in the bibliography, indicate that the measurement of lead concentrations alone can show differences in the levels of lead loading in various reservoirs but that this information is insufficient to pinpoint the actual sources of the lead. The stable isotope abundance patterns of lead, on the other hand, can be used under favourable circumstances to identify sources of the lead and the mixing proportions of different sources experienced by different sinks.

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8. CONCLUDING REMARKS

In an ideal case, stable isotopes can be used as tracers when it is known that there are two sources of the element in question both of which have distinct isotopic signatures. The contribution of these two sources at any given locale can then be estimated from the measured intermediate isotopic composition resulting from the mixing of the sources.

While there are well known point sources of anthropogenic atmospheric sulphur that impinge upon the Great Lakes Basin (Sudbury and Wawa, for example), there is also a contribution to atmospheric sulphur that represents a smeared out average of the individual contributions of many sources. This is demonstrated clearly by the precipitation studies discussed in Section 5 previously. Nriagu and Coker concluded that they were able to distinguish between biological and anthropogenic contributions to the sulphur in precipitation within the Great Lakes Basin. The anthropogenic component though, could not be said to show local variations in isotopic composition reflecting inputs from local sources.

Similarly, in an ideal case, estimates made on the basis of differences in isotopic composition of the relative contributions from different sources, require that these sources have isotopic signatures that are clearly distinct. The lake water study discussed in Section 6 previously, showed that the various inputs and outflows involved in the water balance of Lake Erie all have sulphur isotopic compositions that are rather similar.

There is no doubt that anthropogenic sulphur is a major component of sulphur in lake water and precipitation within the Great Lakes Basin. In practical terms, the reduction of sulphur loading requires ways of identifying the sources of the sulphur present at particular locations. The use of stable isotopes as tracers of such sources clearly has potential, but it is also clear that the simultaneous use of isotope studies of more than one element has greater promise.

Thus, the measurement of $\delta^{34}S$ values of sulphur in precipitation in the Great Lakes Basin has already been shown to be an indicator of the relative amounts of bacteriogenic and anthropogenic sulphur. Simultaneous measurement of oxygen isotopes in sulphate found in precipitation should permit a further distinction to be made between primary and secondary sulphate.

Further, the measurement of lead isotope ratios in water samples should give information on the sources of the lead, which will then in turn add information to the knowledge gained from other stable isotope measurements.

The identification of the sources of atmospheric pollution is a complex problem. The use of stable isotopes as tracers of sources of pollution offers information that is not obtainable from concentration measurements alone. Furthermore, the information obtainable from the simultaneous measurement of isotope ratios in two or more elements increases proportionately information on pollution sources.

The studies of sulphur isotopes in the waters of Lake Erie and in precipitation in the Great Lakes Basin have yielded useful information. In order to maximize the information obtainable from stable isotope measurements, it will be necessary to extend the scope of such measurements.

Seasonal and sporadic variations in sulphur concentration and sulphur isotopic composition at a number of stations should be made on:

sulphur compounds in air samples;
sulphur compounds in aerosols;
sulphur compounds in particulate matter;
sulphur compounds in precipitation;
sulphur compounds in streams, rivers and lakes.

These measurements should be supplemented, by measurements of oxygen isotopic compositions. Sampling stations should be chosen to represent urban, rural and remote areas, as well as a number located in areas where localized sources are known to exist. All of these measurements can be supplemented by lead isotope meaurements.

Further information can be obtained from studies of sediments, both in the Great Lakes and in the smaller lakes within the Basin. Nriagu (personal communication) and Thode (personal communication), are both carrying out studies, on a relatively small scale as yet, in which sulphur isotope variations in sediments are being used to estimate historical patterns of sulphur loading.

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